RESEARCH PROPOSAL

NO. 1612

FOR

A GROUP-SPONSORED COOPERATIVE RESEARCH PROJECT

ON

INCREASED YIELDS IN ALKALINE PULPING

February 12, 1970

TABLE OF CONTENTS

"Increased Yields in Alkaline Pulping"

INTRODUCTION -- AN INDUSTRY CONCERN

For a number of well known reasons, the kraft pulping process has become the dominant pulping process on the North American continent. Although the kraft industry has grown in magnitude, pulping conditions by the kraft process have changed very little from those extant 50 years ago. Furthermore, a majority of the progressive changes in the kraft process have resulted from empirical approaches, and fundamental knowledge has played a relatively small role in the dramatic rise of the process to its dominant position. An excellent review by Peder Kleppe of the status of kraft pulping has just appeared as the Tappi Feature Review for January, 1970 (1). This review is well documented with references to original scientific papers in all aspects of the field of kraft pulping.

Notwithstanding the proven success of the kraft pulping process, the process is still plagued by low yields, a factor which is becoming a great concern to kraft producers, especially in this time of rising pulpwood prices and, in some parts of the country, of lower pulpwood quality. The effect on pulp yield of such obvious parameters as Kappa number, alkalinity, sulfidity, chip size, maximum pulping temperature, and wood quality have been investigated in great detail, both individually and in combination, and pulping conditions are usually chosen to give the highest yield of desired pulp as inexpensively as possible. In spite of the fact that the carbohydrate contents of pulpwoods are approximately 75%, average kraft pulp yields are about 45%. Both cellulose and hemicelluloses are included in this tremendous loss of carbohydrate material.

The major decrease in pulp yield has been attributed to the instability toward alkali of carbohydrates with reducing (carbonyl) end groups resulting in a breakage of glycosidic bonds to give the so-called "peeling reaction." In addition to this shortening of polysaccharide chains by the "peeling reaction", there is a "cleavage" of glycosidic bonds by alkali alone in the absence of activating carbonyl groups.

Inasmuch as an excess of alkali is required for delignification in the kraft pulping process, modifications to the process have been based on the prevention of degradation of polysaccharides, especially hemicelluloses, caused by this excess alkali. Since the degradation has been attributed to the "peeling reaction" initiated by carbonyl end groups, attempts at yield increases have been aimed at the stabilization of these carbonyl end groups. Thus, the reduction of the carbonyl groups to relatively nonsensitive hydroxymethyl groups has been tried with such agents as

sodium borohydride, and oxidation to stable carboxyl groups by such means as polysulfide pulping. Another approach has been to decrease the excess alkali in the system by employing hydrogen sulfide pretreatment under weakly alkaline conditions. Of these, only the polysulfide and hydrogen sulfide processes have been suggested for industrial use. Yield increases ranging from 1 to 7% have been claimed for these modified processes under certain conditions, but under most industrial conditions, the yield increases are just a few percent. Even these few percent represent an enormous amount of kraft fiber when the present and future production of kraft pulp are considered, but these increases account for only a small fraction of the potential carbohydrate pulp available in the wood furnish for the kraft industry. With the continuing rising cost of pulp production, and especially with anticipated increases in the immediate future due to antipollution measures, increased pulp yields from wood raw material have become a great concern to the pulp industry.

EXPERIENCE AND FACILITIES

This concern of the kraft pulp industry for increased yields has been shared by scientists at The Institute of Paper Chemistry. For a number of years individual investigators on our staff have applied themselves to various aspects of the general problem of increased pulp yield in kraft processing. Dr. John Green has pursued a continuing research program on the reaction of cellulose and lower molecular weight carbohydrates with alkali under a variety of conditions including studies on the reaction products; Dr. Norman Thompson has investigated hemicelluloses under similar conditions and has investigated specifically the "peeling reaction"; Dr. Gordon Nicholls has been concerned with the reactions of pulps with alkali and oxygen and with industrial kraft pulping; Dr. Leland Schroeder has studied the reaction of cellulose model carbohydrates with oxygen in alkaline solution; Mr. Harold Swenson has studied molecular properties of celluloses and hemicelluloses; and Dr. Irwin Pearl has studied delignification under various conditions of kraft pulping.

The recent reorganization of the Institute into interdisciplinary, mission-oriented Divisions has brought together all of this experience on alkaline reactions of cellulose and carbohydrates and interest in increasing pulp yields in alkaline pulping. This combination of individual capabilities in the field has suggested a concerted experimental attack on the fundamental processes underlying kraft pulping in order to obtain a more adequate basis for developing industrial modifications for the production of kraft pulp in substantially increased yields. The need for this information will become obvious from reading the BACKGROUND section of this proposal. The availability of and experience with recently introduced sophisticated instrumentation in literally all areas of relevant research adds to the capabilities of our staff to undertake the proposed research.

STATEMENT OF THE PROBLEM

As noted in the INTRODUCTION and as emphasized in Kleppe's review (1), the approaches to increased yields in kraft pulping have been empirical and based on a minimum amount of fundamental research. This small amount of research on the effect of alkali on simple sugars and polysaccharides at temperatures ranging from 20°C. to 170°C. is reviewed in the BACKGROUND portion of this proposal and demonstrates that we have only a scanty knowledge of the rates of alkaline degradation of the glycosidic bonds of polysaccharides and simpler compounds at elevated temperatures and the effect of alkali concentration and other conditions on these rates. The failure of process modifications based on the "peeling reaction" mechanism alone to raise substantially the practical yield of pulp fiber in the kraft process points up the necessity of obtaining a better insight into the several competing reactions taking place in the digester during kraft cooking. The meager experimental data underlying the "peeling reaction" hypothesis makes even this proposed mechanism suspect. Practical modifications to the kraft pulping process to give consistently higher yields of kraft fiber can be evolved only with a knowledge of these digester reactions. It is the purpose of this proposed research program to provide such fundamental knowledge.

BACKGROUND

The mechanism of the "peeling" process and an accompanying slower "cleavage" of glycosidic bonds has received relatively little study. The "peeling reaction" was reported originally in 1955 by investigators at the British Rayon Research Association who were concerned with textile treatments and who studied qualitatively the reaction of a tetrasaccharide under mild alkaline conditions of 0.04N lime water at 25°C. (2), and demonstrated the successive peeling of glucose units. The reaction of alkali on model polysaccharides was then investigated in our laboratories by Dr. Green who employed strong sodium hydroxide solutions and temperatures up to 100°C. and identified the acidic reaction products (3). The acidic reaction products were then found in representative kraft black liquors (4). This work has been continued very recently to include the analysis of neutral products formed during the "peeling" of a disaccharide in normal sodium hydroxide solution at 25°C. (5). The last study also incorporated kinetic data which proved that disaccharides containing only glucose units "peeled" much faster than those containing a mannose unit. This concurs with earlier results indicating the relatively slow "peeling" of hemicelluloses containing glucomannan units (6).

Very little work has been done on the "peeling" reaction at higher temperatures. Lindberg and coworkers (7) did investigate the effect of dilute alkaline solutions (0.02N) on disaccharides containing glucose, mannose, and xylose units at 60° and 75°C., but no one has demonstrated that the "peeling" reaction actually occurs under the conditions of the kraft pulping process -- 2N sodium hydroxide at 170°C. Although studies have been made in our laboratories (8-10) and elsewhere on the "cleavage" of glycosidic bonds under the conditions of kraft pulping, no one has explored the much faster "peeling" reaction under these conditions. Our knowledge of this reaction has been obtained from studies with dilute alkali at low temperatures, and any application of the "peeling" reaction to the conditions of the kraft cook must assume that the same mechanism applies under the more drastic conditions of concentration and temperature. Thus, an extension of earlier studies on the "peeling" reaction to higher temperatures and stronger alkali concentrations would supply extremely valuable fundamental information on the reactions taking place during kraft pulping.

No data are available on the relative rates of the "peeling" reaction and the glycosidic "cleavage" reaction under similar temperature conditions. Best and Green (9) found a rate constant of 0.025 $hr.^{-1}$ for the "cleavage" of the glucose-glucose bond in a protected cellobiose unit in 2.5N sodium hydroxide at 170°C. MacLaurin and Green (5) found that the breaking by a "peeling" reaction of the same glucose-glucose bond in an unprotected cellobiose took place at the much lower temperature of 22°C. with a rate constant of approximately the same order, 0.065 $hr.^{-1}$. If the rate of "peeling" at the lower temperature is approximately the same as the

rate of "cleavage" at the higher temperature, it is evident that any "peeling" reaction at the high temperature would have an extremely fast relative rate.

It should be noted that a cellulosic polysaccharide with a degree of polymerization of 1,000 will have only one reducing end group (where "peeling" can occur) for every thousand glycosidic bonds. Therefore, even though the "peeling" reaction is much faster than the glycosidic "cleavage" reaction at a given reaction site, for the whole polysaccharide chain, there is greater opportunity for the slower "cleavage" reaction to occur, and this may offset, to a certain extent, the inherently faster rate of the "peeling" reaction.

The degradation of acidic polysaccharides by alkali is much faster than that of neutral polysaccharides. This subject has been investigated by many experimentors, including Institute staff members (10, 11). The possible reduction of such acidic polysaccharides to neutral products more stable toward alkali has not been explored.

SCOPE OF PROPOSED RESEARCH PROGRAM

The research program proposed herein is the first part of a long-range program which will give us a better understanding of the effect of kraft pulping conditions on polysaccharides present in wood so that we can evolve pulping condition modifications for the prevention of degradation and solubilization of these carbohydrate components. The first part of this long-range program itself comprises four phases as follows:

1. Establishment of the rates of "peeling" and of "glycosidic cleavage" of model disaccharides under conditions approaching those of commercial kraft pulping. Results will demonstrate whether the "peeling" reaction is actually the major factor in the degradation of polysaccharides during kraft pulping as assumed heretofore, or whether the "cleavage" of glycosidic linkages is the deciding factor. Recent failures of end group modifications to increase substantially the carbohydrate pulp yields suggest enlightening results from this phase.

2. A study of various buffers at pulping temperatures including the determination of their pH values and their catalytic effects on either the "peeling" or "glycosidic cleavage" reactions.

3. The extension of this study to soluble polysaccharides to determine whether the cleavage of a single glycosidic bond in a model disaccharide is similar to that of several glycosidic bonds in a polysaccharide.

4. The study of insoluble cellulose and hemicellulose polysaccharides in heterogeneous systems to determine if the rate of degradation is diffusion controlled or whether the degradation is controlled by either the rate of "peeling" or of "glycosidic cleavage".

The results of these four fundamental phases will establish a firm basis for the development of modifications to kraft cooking conditions in order to prevent major losses of polysaccharide pulp.

Phase One

Phase One will be concerned primarily with a kinetic study of homogeneous systems in alkali comprising solutions of disaccharides containing glucose, mannose, and xylose units--units found in cellulose and hemicelluloses from both softwoods and hardwoods. Conditions employed in these kinetic studies would include sodium hydroxide concentrations as high as 2N in strength, and concentrations of alkali and carbohydrate will be such that the alkali is always in great excess. Other alkalies such as sodium sulfide will be considered.

With excess alkali as noted, the rate of "peeling" will be a function of the concentration of reducing end groups. Concentrations of end groups of cellulose under conditions of kraft cooking are necessarily low. Thus, a cellulose with a degree of polymerization of 1,000 would require a suspension of 162 grams per liter of alkaline solution to give a 0.001 molar concentration of reducing end groups, and this is a high consistency of cellulose fibers. Hemicelluloses with lower degrees of polymerization would require somewhat less weight per liter of alkaline solution to give a 0.001 molar concentration. Our earlier kinetic studies on model disaccharides at low temperature were performed at molar concentrations of 0.001 (5). We plan to employ 0.001 molar concentrations for the first studies in this program because this low concentration of reducing end group will help offset the exceptionally high reaction rate expected at the higher temperatures we will employ. As temperatures are increased, it will be necessary to design and build flow reactors for rapid mixing and rapid sampling in order to obtain the kinetic data. A reactor for homogeneous systems at temperatures up to 100°C. for use at atmospheric temperature will be built for the first experiments, and results obtained in these experiments will lead to the design of a second reactor for use with either homogeneous or heterogeneous systems up to kraft pulping temperature of 170°C.

Phases Two, Three, and Four

The results, experience, and expertise obtained during Phase One of this program will enable us to outline successive phases in more detail later in the program.

Starting Materials

In Phase One of this study, emphasis will be on more readily available model disaccharides. Cellobiose is available commercially. Xylobiose and mannobiose will be prepared by graded hydrolysis of polysaccharides. Glucosylmannose will be prepared from cellobiose. If experimental results suggest studies on ketose intermediates, cellobiulose will be prepared, but only in small amounts as necessary.

LITERATURE CITED

1. Kleppe, P. J., Tappi 53, no. 1:35 (1970).

2. Corbett, W. M., and Kenner, J., J. Chem. Soc. 1955:1431.

3. Green, J. W., J. Am. Chem. Soc. 78:1894 (1956).

4. Green, J. W., Tappi 39, no. 7:472 (1956).

5. MacLaurin, D. J., and Green, J. W., Can. J. Chem. 47:3947, 3957 (1969).

6. Casebier, R. L., and Hamilton, J. K., Tappi 48, no. 11:664 (1965).

7. Lindberg, B., Theander, O. and Uddegard, J., Svensk Papperstidn. 69:360 (1966).

8. Brooks, R. D., and Thompson, N. S., Tappi 49, no. 8:362 (1966).

9. Best, E. V., and Green, J. W., Tappi 52, no. 7:1321 (1969).

10. Robbins, J. H. and Green, J. W., Tappi 52, no. 7:1346 (1969).

PROJECT DIRECTION

The research program as herein proposed will go forward in the Chemistry Group Laboratories of the Division of Natural Materials and Systems and will be under the general supervision of Dr. Irwin A. Pearl, Group Coordinator. Technical supervision of the program will be the responsibility of Dr. John W. Green, Project Leader, with whom you may correspond directly concerning progress of the work. Dr. Green has been responsible for most of the previous work in this field in our laboratories. Assisting Dr. Green will be Dr. Leland R. Schroeder who has worked extensively in the fields of carbohydrate reaction kinetics and in the synthesis of carbohydrate derivatives and Dr. John F. Perry representing our engineering and computer disciplines.

FACILITIES AVAILABLE FOR THIS RESEARCH

Extensive laboratories are available at the Institute for conducting the proposed program. Facilities include all types of sophisticated instrumentation for research in analytical, organic, and physical chemistry of carbohydrates such as analytical and preparative gas chromatographs, infrared, ultraviolet, nuclear magnetic resonance, and laser Raman spectrometers, and Auto-Analyzer system. In addition, complete instrumentation for molecular weight determinations is available. Besides specific pieces of equipment associated with this research, the Institute, of course, is equipped generally for all types of chemical, physical, and biological research on pulp and paper products, processes, and fibrous raw materials. Specific equipment necessary for the proposed program and not at hand are the flow reactors for rapid reaction and a commercially available instrument for the determination of pH of alkaline systems at high temperatures.

REPORTS

The Institute shall render technical reports at the end of each six-month period throughout the course of the project. In addition, informal reports or memoranda may be submitted at interim periods as the progress of the work so dictates.

BUDGET AND TIME SCHEDULE

The research program as herein set forth is planned for a two-year effort, and the scheduling of research activity in the Division of Natural Materials and Systems is such that the Institute is in a position to commence the research rather shortly after a number of companies have authorized their participation in the group research to afford a reasonable budgetary level for the project. The research program is such that it can be pursued at various levels of activity, and the total amount of research accomplished will be dependent upon the total budget available. The Institute would prefer to have a budget in the neighborhood of $50,000 per year for the two-year period, but it feels that it can undertake the program and, in view of its readiness for research in this field, it can accomplish some significant progress if it is provided a budget of about $30,000 per year for the two-year period, or a total of $60,000. The desired level, of course, will be obtained quite likely if sufficient number of companies support the work and certainly will be appropriate in the light of the personnel and the facilities available for the research.

SHARE OF THE BUDGET

Each participating member company's share of the budget will relate to the size of the company by a formula based upon the company's Institute membership dues. This approach is in keeping with some of the previous group projects in this field. Therefore, we have established three levels of participation; namely, $5,400 per year, $3,600 per year, and $1,800 per year; and each participating member company's share per year will be $5,400, $3,600, or $1,800, depending upon your Institute's annual membership dues in accordance with the following schedule:

Your annual dues range	One Year Share	Two Year Total Share
$25,000 and over	$5,400	$10,800
$10,000 - $25,000	$3,600	$ 7,200
less than $10,000	$1,800	$ 3,600

The appropriate amount for each member company is set forth in the Authorization Form Letter.

AUTHORIZATION AND ESTABLISHMENT OF PROJECT

This proposal is available to member companies of the Institute and will be sent to those who have an interest in the program. An Authorization Form Letter is being submitted in duplicate to each company receiving this proposal. If your company wishes to join the group research project described above, please execute and complete this form letter (retaining one copy for your files); this will constitute your authorization to participate in and support this research providing similar authorizations are received from other companies sufficient to attain the desired budgetary level. The Institute will establish the project and commence the research. It is hoped that member companies will forward their executed form letters as soon as possible in order that the work can be initiated without delay.

JOINING THE RESEARCH PROJECT

After the project is established, companies may join the project at a later date by signing the appropriate Authorization Form Letter and paying their shares of the cost as set forth above. The support from such additional companies may reduce proportionately the budgetary share of the individual participants depending upon the level of activity.

COMPANY TECHNICAL REPRESENTATIVE

Each participating company shall designate a qualified technical representative who will attend the meetings and will also be available for liaison and consultation with the Institute.

PATENTS

The purpose of this program is to advance scientific insights and understanding in the area of alkaline pulping and it is not contemplated, therefore, that the Institute or any of the participating companies in the program will be concerned with the patenting of any discoveries or inventions. However, it is conceivable that the

Institute as a participating company may deem it advisable to seek patents for the purpose of protecting certain work as for the purpose of keeping fields "open". In such event, the Institute shall have exclusive right to said patents and shall further grant to all the initial and/or subsequent participating companies in the project a nonexclusive, royalty-free license under said patents.

PUBLICATION

It is understood that if any or all of the participating companies wish to publish, or publicly refer to, the results developed under such cooperative research projects, The Institute of Paper Chemistry reserves the right to edit, and to approve or disapprove, such reports, references, or papers. The Institute shall not publish said results without prior approval of all of the participating companies. However, the Institute shall have the right to publish the results of the investigations and researches after a period of two years from the date of transmittal of the results to the companies participating in the research program, provided that, if the Institute finds after consultation with said companies that publication after the expiration of the two-year period would prove detrimental to the best interest of certain companies, the Institute shall delay such publication a reasonable time.

CONCURRENT RESEARCH

It is understood that the Institute and/or any or all of the participating companies shall have the privilege of carrying on similar, related, or collateral research and investigations concurrently on their own behalf or for companies or organizations having similar objectives and interest in the field covered by the proposed program.

CONTINUATION OF RESEARCH

If it is decided that this proposed research will not be pursued after the termination of this project, the Institute reserves the right to pursue the particular investigation and research itself, or if the occasion arises, to pursue such investigation and research in cooperation with others. The Institute shall have the right to use or otherwise refer to, any information developed on this proposed research project in connection with any continued research in this area whether an extension of the same project or the initiation of a related project or projects. This right, however, shall

not be exercised so as to derogate from the rights of the participating companies which may accrue under "Patents" and "Publications" above.

INVOICING PROCEDURES AND CHARGES

The Institute of Paper Chemistry is a nonprofit organization and as such our charges are based upon the actual cost of the work performed plus 15% for indirect expenses. Invoices are submitted every month while the work is in progress, and cover personal services, use of equipment, disbursements for supplies, samples, telephone and other out-of-pocket expenses, and the 15% indirect service charge on personal services. Any equipment necessary for a cooperative research project not already a part of the Institute's facilities is to be provided by participating companies at their expense and will remain a part of the Institute's facilities upon termination of the project.

MEMBERSHIP RESERVE ACCOUNT

The balance accumulated in your reserve account will be utilized to defray the personal services charges in connection with this project. The disbursements and the indirect service charge will be billed for cash payment. If the balance in the member's reserve account becomes exhausted during the period of the membership agreement or is "expired" at the termination of the membership agreement pursuant to such agreement, the member company, of course, would be billed for cash payment for the personal services charges also.